

Statistical Ensembles

How do we make connection between thermodynamics and mechanics?

Ergodic hypothesis

Consider a system of N particles, each with three degrees of freedom, x, y, z . The system is described, in Hamiltonian classical mechanics, by $6N$ canonical variables

$$q_1, q_2, \dots, q_{3N}, p_1, \dots, p_{3N}$$

Hamilton's eqns
$$\begin{aligned} \dot{q}_i &= \frac{\partial H}{\partial p_i} \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i} \end{aligned} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} i=1, \dots, 3N$$

give the trajectory of the system $\{q_i(t), p_i(t)\}$ in "phase space" - a $6N$ dimensional space whose coordinates are the q_i and p_i .

In general, ^{total} energy will be conserved as the system moves ~~assuming there are no external time~~ ~~regions~~. The condition $H[q_i, p_i] = E$ defines a $6N-1$ dimensional surface in phase space on which the system's trajectory is confined.

If one wanted to compute the ~~average~~ ^{measured} value of some quantity, averaged over an interval of time τ , it is:

$$\langle f \rangle = \frac{1}{\tau} \int_{t_0}^{t_0 + \tau} dt f[q_i(t), p_i(t)]$$

In general, for large N , we expect the trajectory to be some horribly complicated curve on the constant energy surface, that we have no way of computing directly.

To compute $\langle f \rangle$ we therefore need to make an assumption. The ergodic hypothesis says: during any time interval τ , ~~this~~ sufficiently long, the location of the system in phase space $\{q_i(t), p_i(t)\}$ is equally likely to be anywhere on the surface of constant energy E .

$$\text{Therefore } \langle f \rangle = \int dq_i dp_i f[q_i, p_i] \rho(q_i, p_i)$$

$$\text{where } \rho(q_i, p_i) = C \delta(H[q_i, p_i] - E)$$

where C is a normalizing factor such that $\int dq_i dp_i \rho[q_i, p_i] = 1$

ρ is called the density matrix.

with the above form, ρ is called the microcanonical ensemble

The ergodic hypothesis cannot in general be proven. But the existence of thermodynamics, as an empirically consistent theory, suggests why it may be true.

① Liouville's Theorem (see later)

② By thermodynamics we assume that the macroscopic properties of a system are completely described by a set of a few macroscopic variables, such as total energy E , N , V , μ . If the ergodic hypothesis were not true, there would be parts of phase space with the same value of E , that never "saw" each other - i.e. a trajectory in one part would not enter the other, ad vice versa. One could imagine, therefore, that systems in these two disjoint regions of phase space might have different properties, i.e. have different time averages of some particular property $f(q, p)$. One therefore might expect them to represent thermodynamically distinguishable states. But this would contradict the assumption that E alone is the important thermodynamic variable.

Alternatively, if ergodicity fails, there might be some other important macroscopic variable (for example magnetization) which one overlooked.

The disjoint regions of the constant energy surface could correspond to different values of this new macroscopic variable.

In other words, in the absence of any further information, we assume that all microscopic states $\{q_i, p_i\}$ consistent with a given set of macroscopic thermodynamic variables, E, N, V , are equally likely.

In the ensemble theory one abandons any effort to compute thermodynamic properties from the explicitly time dependent trajectory of the system in phase space. Rather one describes the thermodynamic state as represented by a particular ensemble given by the density matrix $\rho(q_i, p_i)$

The ensemble average $\langle f \rangle = \int dq_i dp_i f(q_i, p_i) \rho(q_i, p_i)$ is the value one would find not for a single isolated system moving on its trajectory, ~~but for a collection~~ but for the average of a collection of systems distributed in phase space according to the density ρ . The ergodic hypothesis asserts these two types of averages are equal.

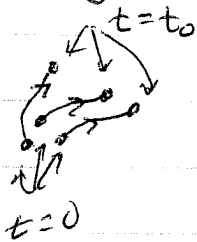
$\rho(q_i, p_i)$ can be viewed as the probability density that the system will be found in phase space at $\{q_i, p_i\}$

Equilibrium is described by a density matrix that does not vary in time.

Liouville's theorem

The concept of density matrix will soon be expanded beyond the particular example of the microcanonical ensemble. It can also be generalized to non-equilibrium situations. $\rho(q_i, p_i, t)$
We therefore want to see what general condition ρ must satisfy in order that $\frac{\partial \rho}{\partial t} = 0$, i.e. steady-state

Consider an initial density ρ of points in phase space. As the systems represented by these initial points evolve in time, their trajectories give the density $\rho(t)$ at later times. Think of the points in ρ like particles in a fluid.



The probability density ρ must obey a local conservation equation

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) = 0$$

where \vec{v} is the "velocity" vector of the probability "current" $\rho \vec{v}$, that tells how the points in ρ flow in phase space.

\vec{v} is the $6N$ dimensional vector $(\dot{q}_1, \dots, \dot{q}_{3N}, \dot{p}_1, \dots, \dot{p}_{3N})$

and

$$\begin{aligned} \vec{\nabla} \cdot (\rho \vec{v}) &= \sum_{i=1}^{3N} \left[\frac{\partial}{\partial q_i} (\rho \dot{q}_i) + \frac{\partial}{\partial p_i} (\rho \dot{p}_i) \right] \\ &= \sum_{i=1}^{3N} \left[\frac{\partial \rho}{\partial q_i} \dot{q}_i + \rho \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \rho}{\partial p_i} \dot{p}_i + \rho \frac{\partial \dot{p}_i}{\partial p_i} \right] \end{aligned}$$

$$\vec{\nabla} \cdot (f \vec{v}) = \sum_i \left[\frac{\partial f}{\partial g_i} \dot{g}_i + \frac{\partial f}{\partial p_i} \dot{p}_i \right] + f \left[\frac{\partial \dot{g}_i}{\partial g_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right]$$

use $\dot{g}_i = \frac{\partial H}{\partial p_i}$ $\dot{p}_i = -\frac{\partial H}{\partial g_i}$

$$\Rightarrow \frac{\partial \dot{g}_i}{\partial g_i} = \frac{\partial H}{\partial p_i \partial g_i} \quad \frac{\partial \dot{p}_i}{\partial p_i} = -\frac{\partial H}{\partial g_i \partial p_i}$$

so $\frac{\partial \dot{g}_i}{\partial g_i} + \frac{\partial \dot{p}_i}{\partial p_i} = 0$

and

$$\vec{\nabla} \cdot (f \vec{v}) = \sum_i \left\{ \frac{\partial f}{\partial g_i} \frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial H}{\partial g_i} \right\}$$

= $[f, H]$ ← defines the "Poisson bracket"

so

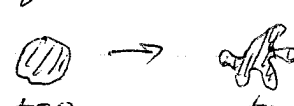
$$\frac{\partial f}{\partial t} + [f, H] = 0$$

$$\Leftrightarrow \frac{\partial f}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial f}{\partial g_i} \frac{dg_i}{dt} + \frac{\partial f}{\partial p_i} \frac{dp_i}{dt} \right\} = \frac{df}{dt} = 0$$

↑
total time derivative

$\frac{df}{dt}$ is also called the convective derivative. It is how f changes in time if one moves along with "particles" (i.e. the systems on their trajectories)

$\frac{df}{dt} = 0 \Rightarrow$ density in phase space is ~~independent~~ ^{constant} in time as it flows - like an incompressible fluid.

 $t=0 \rightarrow t$ density of points

Equilibrium requires a stronger condition, namely $\frac{\partial \rho}{\partial t} = 0$,
 so that ensemble averages will not vary in time.

$$\frac{\partial \rho}{\partial t} = 0 \Rightarrow [\rho, H] = 0$$

$$[\rho, H] = \sum_i \left[\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right]$$

we see that $[\rho, H] = 0$ if $\rho(q_i, p_i)$ depends
 on q_i, p_i only via the function $H[q_i, p_i]$, i.e.

$\rho = \rho(H(q_i, p_i))$. Then $\frac{\partial \rho}{\partial q_i} = \frac{\partial \rho}{\partial H} \frac{\partial H}{\partial q_i}$, $\frac{\partial \rho}{\partial p_i} = \frac{\partial \rho}{\partial H} \frac{\partial H}{\partial p_i}$

$$[\rho, H] = \sum_i \left[\frac{\partial \rho}{\partial H} \frac{\partial H}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial H} \frac{\partial H}{\partial p_i} \frac{\partial H}{\partial q_i} \right] = 0$$

so $\rho(q_i, p_i)$ must be constant on constant
 energy surfaces, if ρ is to describe equilibrium.

We already saw one example

microcanonical ensemble $\rho(q_i, p_i) \sim \delta(H(q_i, p_i) - E)$

another choice later will be

canonical ensemble $\rho(q_i, p_i) \sim e^{-H[q_i, p_i]/k_B T}$

Microcanonical Ensemble and Entropy

We saw that the microcanonical ensemble, at energy E , assigned equal weight to all systems on the surface in phase space of constant energy $H[q_i, p_i] = E$.

To count the number of such states on the energy surface we define the "density of states"

$$g(E) \equiv \int \frac{dq_i dp_i}{h^{3N}} \delta(H[q_i, p_i] - E)$$

(number of states per unit energy)

where h is a constant with units of $q_i p_i$. h^{3N} represents the volume of phase space occupied by one "state". Classically, h is totally arbitrary so our thermodynamic results should not depend on it. Quantum mechanically, we will see that h turns out to be Planck's constant.

At this stage, the factor $\frac{1}{h^{3N}}$ is introduced so that $g(E)$ has the units of $1/\text{energy}$.

We can now define the number of states in a shell of thickness Δ about the energy surface E .

$$\Omega(E, V, N) = \int_{E-\frac{\Delta}{2}}^{E+\frac{\Delta}{2}} dE' g(E')$$

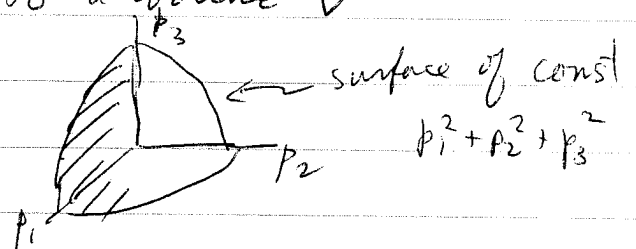
Ω is a pure number. Again, Δ is arbitrary, but

$$\frac{E}{N} \ll \Delta \ll E$$

assumed to be ~~small~~. It can be thought of as representing the finite accuracy with which one knows E . Our thermodynamic results should not depend on Δ . [both \hbar and Δ are introduced so that ~~the~~ ~~dimension~~ of Ω is a dimensionless pure number that we can think of as being the ~~total~~ number of microscopic states occupied in the microcanonical ensemble at E]

Example: Compute Ω for the ideal gas of non interacting particles, confined to a volume V

$$H = \sum_{i=1}^N \frac{|\vec{p}_i|^2}{2m}$$



$$\begin{aligned} g(E) &= \prod_{i=1}^N \int \frac{d^3 p_i}{h^{3N}} \delta\left(\sum_i \frac{|\vec{p}_i|^2}{2m} - E\right) \\ &= \frac{V^N}{h^{3N}} \prod_{i=1}^N \int d^3 p_i \delta\left(\sum_i \frac{|\vec{p}_i|^2}{2m} - E\right) \end{aligned}$$

The surface of constant energy is just the surface of a sphere in $3N$ dimensional momentum space given by the coords $p_{1x}, p_{1y}, p_{1z}, \dots, p_{Nx}, p_{Ny}, p_{Nz}$. The radius of the sphere is $\sqrt{2mE}$.

Let $P \equiv \sqrt{\sum_{i=1}^N |\vec{p}_i|^2}$ be the length of the momentum vector in the $3N$ dimensional momentum space.

Then $\prod_{i=1}^N d^3 p_i = dP P^{3N-1} d\Omega_{3N}$

\uparrow differential solid angle
in $3N$ dimensional space

$$g(E) = \frac{V^N}{h^{3N}} \int d\Omega_{3N} \int_0^{\infty} dP P^{3N-1} \delta\left(\frac{P^2}{2m} - E\right)$$

$$= \frac{V^N}{h^{3N}} S_{3N} \int_0^{\infty} dP P^{3N-1} \frac{\delta(P - \sqrt{2mE})}{(P/m)}$$

\uparrow
area of unit
sphere in $3N$ -dim space

\leftarrow from
converting the
 δ -function

$$\delta(f(x)) = \frac{\delta(x)}{f'(x)}$$

$$= \frac{V^N}{h^{3N}} S_{3N} m (2mE)^{\frac{3N-2}{2}}$$

From Appendix C of Pathria (eqn C.76) or elsewhere,
one has the area of unit sphere in d -dim space

$$S_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}$$

where $\Gamma(n) = (n-1)!$

for integer n

Γ is the Gamma function

So $S_{3N} = \frac{2\pi^{3N/2}}{(\frac{3N}{2}-1)!}$

$$g(E) = \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{(\frac{3N}{2}-1)!} m \frac{(2mE)^{\frac{3N}{2}}}{2mE}$$

$$g(E) = \frac{V^N (2\pi m E)^{3N/2}}{h^{3N} \left(\frac{3N}{2} - 1\right)!} \frac{1}{E}$$

$$\Omega(E) = \int_{E-\frac{\Delta}{2}}^{E+\frac{\Delta}{2}} dE' g(E') \approx g(E) \Delta$$

$$\Omega(E) = \frac{V^N (2\pi m E)^{3N/2}}{h^{3N} \left(\frac{3N}{2} - 1\right)!} \frac{\Delta}{E}$$

For large N , $\Omega(E)$ is a very rapidly increasing function of E ! $\sim E^{\frac{3N}{2}-1}$

We will now argue that $\Omega(E)$ is related to the entropy of the system.

Consider two sub-systems separated by a wall

E_1	E_2
V_1	V_2
N_1	N_2

$$E_T = E_1 + E_2 \quad \text{energy conserved}$$

let $g_1(E_1)$ is density of states of system 1 with energy E_1
 $g_2(E_2)$ is density of states of system 2 with energy E_2

Now suppose the wall is thermally conducting so that energy can be transferred between the two systems. $\Rightarrow E_1$ can vary but $E_T = E_1 + E_2$ is fixed. What will be the value of E_1 when the system comes to equilibrium?